

Appl. No. : 09/037,945
Filed : March 10, 1998

Claims 1, 4 and 5 of this application were provisionally rejected under the judicially created doctrine of obviousness-type double patenting over claims 1, 4 and 5 of copending application 08/565,991. As this rejection was provisional, no action is required at this time.

Claims 1,2,4,8,9 and 14-17 were rejected as anticipated by German Patent 266885. That patent teaches the use of a wet and dry oxidation, in sequence, and does not suggest the omission of the wet oxidation step. The claims now require that the oxidation be hydrogen-free, and there is no suggestion in the German reference to eliminate hydrogen from the etch. Moreover, even the "dry" etch is carried out with "a small amount of hydrogen chloride or chlorocarbon gas added". This teaches directly away from a "hydrogen-free" process, since the chlorocarbon gas used in dry etches is most typically HCl gas, as shown in the Richard C. Dorf Electrical Engineering Handbook and the McGraw-Hill Practical Guide to Semiconductor Processing, which documents were brought to the Applicants' counsel's attention, and are attached to this Amendment. In view of this evidence, and the inclusion of wet processing in the German reference, applicant believes that the claims, as amended, are now in a condition for allowance.

Claim 3 was rejected as obvious over the German reference and further in view of Marshall et al and Miyoshi et al. Claim 3 is dependent on Claim 1, and is believed to be patentable in view of the amendment to the parent claim.

Claims 11-13 were rejected as obvious over Marshall et al in view of Sze. As acknowledged by the Examiner, Marshall teaches ultra high pressure oxidation, and this reference is overcome by the limitation in Claim 11 and its dependent Claims 12 and 13 to pressures less than 30 atm..


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Applicants have made a diligent effort to place the claims of this application in a condition for allowance, and respectfully request that this case be passed to issue.

Respectfully submitted,

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Dated: 10/15/99

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Library of Congress Cataloging-in-Publication Data

Van Zant, Peter.

Microchip fabrication : a practical guide to semiconductor processing / Peter Van Zant.—3rd ed.

p. cm.

Includes index.

ISBN 0-07-067250-4 (hardcover)

1. Semiconductors—Design and construction. I. Title.

IN PROCESS

621.3815'2—dc20

96-15729

CIP

McGraw-Hill

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2 3 4 5 6 7 8 9 0 DOC/DOC 9 0 1 0 9 8 7

ISBN 0-07-067250-4

The sponsoring editor for this book was Steve Chapman, the editing supervisor was Fred Bernardi, and the production supervisor was Pamela Pelton. It was set in Century Schoolbook by Dina E. John of McGraw-Hill's Professional Book Group composition unit.

Printed and bound by R. R. Donnelley & Sons Company.



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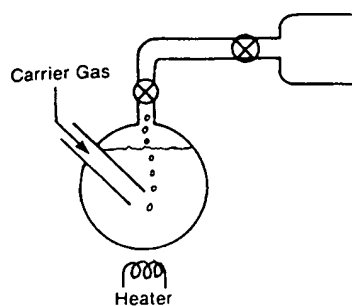


Figure 7.20 Bubbler water vapor source.

liquid. As the carrier gas is bubbled through the water and passes through the vapor, it becomes saturated with water. Under the influence of the elevated temperature inside the tube, the water vapor becomes steam and causes the oxidation of the silicon surfaces.

Drawbacks to bubbler systems are changes in the amount of water vapor entering the tube as the water level in the bubbler changes and fluctuations in the water temperature. With bubblers there is always concern about contamination of the tube and oxide layer from dirty water or dirty flasks. This contamination potential is heightened by the need to open the system periodically to replenish the water.

Flash systems. A *flash system* is also a glass or quartz system (Fig. 7.21). The system is connected to a continuous source of deionized water through a narrow tube designed to allow small drops of the water into the flask. The drops fall onto a heated quartz surface maintained at a high enough temperature to "flash" the drops into steam. A carrier gas also fed into the system takes the steam created into the oxidation tube. Flash systems suffer the same control problems as bubblers but are somewhat cleaner in that they do not have to be replenished with water.

Dry oxidation (dryox). Bubblers and flash systems are adequate for thick and noncritical oxide layers, but new levels of thickness control

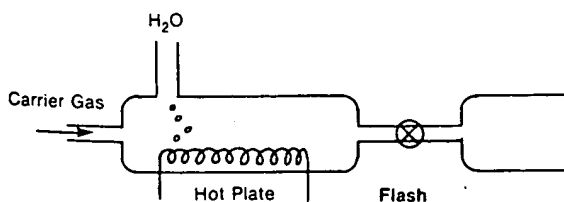


Figure 7.21 Flash system water vapor source.

and cleanliness came with the introduction of MOS devices. The heart of a MOS transistor is the gate structure, and the critical layer in the gate is a thin, thermally grown oxide. Liquid-water-steam systems are unreliable for growing thin, clean gate oxides. The answer was found in dry oxidation (or dry steam) process (Fig. 7.22).

In the dry oxidation system, gaseous oxygen and hydrogen are introduced directly into the oxidation tube. Inside the tube, the two gases mix and, under the influence of the high temperature, form steam. The result is a wet oxidation in steam. Dryox systems offer improved control and cleanliness over liquid systems. First, gases can be purchased in a very clean and dry state. Second, the amounts going into the tube can be very precisely controlled by the mass flow controllers. Dryox is the preferred general oxidation method for production for all advanced devices.

A drawback to dryox systems is the explosive property of hydrogen. At oxidation temperatures, hydrogen is very explosive. Precautions used to reduce the explosion potential include separate oxygen and hydrogen lines to the tube and flowing excess oxygen into the tube. The excess oxygen ensures that every hydrogen molecule (H_2) will combine with an oxygen atom to form the nonexplosive water molecule, H_2O . Other precautions used are hydrogen alarms and a hot filament in the source cabinet and in the scavenger end of the furnace to immediately burn off any free hydrogen before it can explode.

Chlorine-added oxidation. The thinner MOS gate oxides require very clean layers. Improvements in cleanliness and device performance are achieved when chlorine is incorporated into the oxide.¹³ The chlorine tends to reduce mobile ionic charges in the oxide layer, reduce structural defects in the oxide and silicon surface, and reduce charges at the oxide-silicon interface. The chlorine comes from the inclusion of anhydrous chlorine (Cl_2), anhydrous hydrogen chloride (HCl), trichloroethylene (TCE), or trichloroethane (TCA) in the dry oxygen gas stream. The gas sources, chlorine, hydrogen chloride, and oxygen, are metered into the tube from separate flow meters in gas flow controller. The liquid sources, TCE and TCA, are carried into the tube as vapors from liquid bubblers. For safety and ease of delivery, TCA is the preferred source of chlorine. The oxidation-chlorine cycle may take place in one step or be preceded or followed by a dry oxidation cycle.

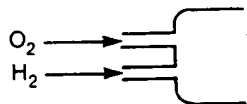


Figure 7.22 "Dryox" (dry steam) water vapor source.

drain Along with the source and gate, one of the three regions of a unipolar or field-effect transistor (FET).

drive-in Stage in diffusion where the dopant is driven deeper into the wafer.

dry etch See **plasma etch**.

dry ox The growth of silicon dioxide using oxygen and hydrogen, which form water vapor at process temperatures, rather than using water vapor directly.

dry oxide Thermal silicon dioxide grown using oxygen.

e-beam (electron beam) An exposure source which allows direct image formation without a mask. An E-beam can be deflected by electrostatic plates and therefore directed to precise locations, resulting in the generation of sub-micron-size patterns.

e-beam aligner An aligner tool that exposes the resist-coated wafer surface by steering (writing) an electron beam across the wafer surface.

e-beam evaporation (electron beam evaporation) Phase change that uses the energy of a focused electron beam to provide the required energy to change solid metal or alloys from solid to gas.

e-beam exposure system A machine in which the image pattern is stored in a computer memory and used to control the electrostatic plates that in turn direct the E-beam, resulting in the generation of patterns without the use of reticles or photomasks.

edge die The incomplete die located on the edge of the wafer.

EEPROM (electrically erasable PROM) A memory circuit with the capability of data erasure and acceptance of new information by the application of an electrical pulse.

electromigration The diffusion of electrons in electric fields set up in the lead while the circuit is in operation. It occurs in aluminum and is exhibited as a field failure, not as a process defect. The metal thins and eventually separates completely, causing an opening in the circuit.

electron A charged particle revolving around the nucleus of an atom. It can form bonds with electrons from other atoms or be lost, making the atom an ion.

ellipsometer Instruments that use laser light sources to measure thin film thickness.

emitter (1) The region of a transistor that serves as the source or input end for carriers. (2) The N-type diffusion usually done using phosphorus, which forms the emitter of NPN transistors, the base contact of PNP transistors, the N+ contact of NPN transistors, and low-value resistors.

epitaxial (Greek for "arranged upon") The growth of a single-crystal semiconductor film upon a single-crystal substrate. The epitaxial layer has the same crystallographic characteristics as the substrate material.

epoxy package See **molded package**.

EPROM (erasable PROM) A memory circuit with the capability of data erasure and acceptance of new information.



THE

Electrical Engineering

HANDBOOK

Editor-in-Chief

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University of California, Davis

CRC PRESS

Boca Raton Ann Arbor London Tokyo

and N_0 in terms of the reaction rate and diffusion coefficient of the oxidizing species. This in turn specifies the flux terms which can be used in the solution of the differential equation:

$$\frac{dx}{dt} = \frac{F}{N_{ox}} \quad (21.3)$$

for the oxide growth, x . In this equation N_{ox} is the number of oxidant molecules per unit volume of oxide. An excellent derivation of the growth equation is given in Grove [1967]. Here we give the result which can be represented by:

$$x_{ox} = \frac{A}{2} \left[\sqrt{1 + \frac{4B}{A^2} (t + \tau)} - 1 \right] \quad (21.4)$$

where x_{ox} is the oxide thickness, B is the parabolic rate constant, B/A is the linear rate constant, t is the oxidation time, and τ represents the initial oxide thickness.

Referring to Eq. (21.4) we see there are two regimes of oxide growth. For thin oxides or short times, i.e., the initial phase of the oxidation process, the equation reduces to:

$$x_{ox} = \frac{B}{A} (t + \tau) \quad (21.5)$$

and the growth is a linear function of time, limited by the surface reaction at the Si/SiO₂ interface.

For thicker oxides and longer times the reaction is limited by the diffusion of the oxidizing species across the growing oxide layer, and the limiting form of Eq. (21.4) is

$$x_{ox} = \sqrt{Bt} \quad (21.6)$$

Oxidation Rate Dependencies

Typical oxidation curves showing oxide thickness as a function of time with temperature as a parameter for wet and dry oxidation of <100> silicon are shown in Fig. 21.2. This type of curve is qualitatively similar for all oxidations. The oxidation rates are strongly temperature dependent as both the linear and parabolic rate constants show an Arrhenius relationship with temperature. The linear rate is dominated by the temperature dependence of the interfacial growth reaction and the parabolic rate is dominated by the temperature dependence of the diffusion coefficient of the oxidizing species in SiO₂.

Wet oxides grow faster than dry oxides. Both the linear and parabolic rate constants are proportional to equilibrium concentration of the oxidant in the oxide. The solubility of H₂O in SiO₂ is greater than that of O₂ and hence the oxidation rate is enhanced for wet oxides.

Oxidation rate depends on substrate orientation [Ghandhi, 1968]. This effect is related to the surface atom density of the substrate, i.e., the higher the density, the faster the oxidation rate. Oxidation rate also depends on pressure. The linear and parabolic rates are dependent on the equilibrium concentration of the oxidizing species in the SiO₂ which is directly proportional to the partial pressure of the oxidant in the ambient.

Oxide growth rate shows a doping dependence for heavily doped substrates (>10²⁰ cm⁻³). Boron increases the parabolic rate constant and phosphorus enhances the linear rate constant [Wolf and Tauber, 1986].

Oxide Characteristics

Dry oxides grow more slowly than wet oxides, resulting in higher density, higher breakdown field strengths, and more controlled growth, making them ideal for metal-oxide semiconductor (MOS) gate dielectrics.

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s can vary consider-
erences [Sze, 1983].
name implies, dry

(21.1)

water at 95°C. Most
s to form steam, and
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(21.2)

in X_0 represents the
a moving boundary.
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he oxide surface, N_3 ,
g incorporated in the
species then diffuses
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interface to form SiO₂.
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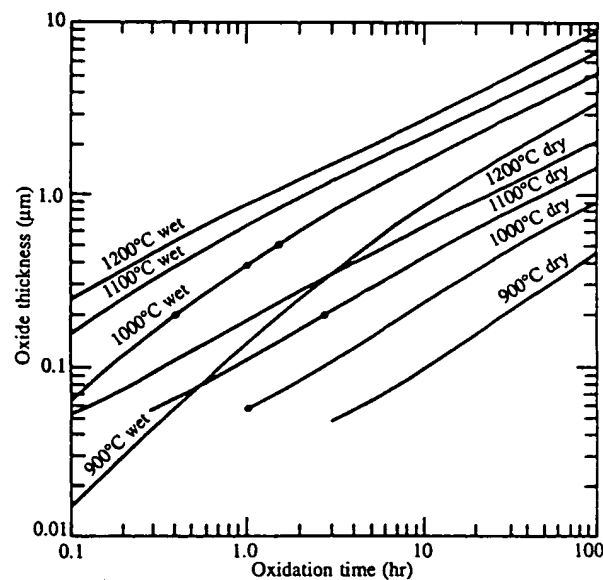


FIGURE 21.2 Thermal silicon dioxide growth on <100> silicon for wet and dry oxides. (Source: R. C. Jaeger, *Introduction to Microelectronic Fabrication*, vol. 5 in the Modular Series on Solid State Devices, G. W. Neudek and R. F. Pierret, Eds., Reading, Mass.: Addison-Wesley, 1988, p. 35. With permission.)

Wet oxidation is used for forming thick oxides for field isolation and masking implants and diffusions. The slight degradation in oxide density is more than compensated for by the thickness in these applications.

<100> substrates have fewer dangling bonds at the surface, which results in lower fixed oxide charge and interface traps and therefore higher quality MOS devices.

Conventional dopants (B, P, As, and Sb) diffuse slowly in both wet and dry oxides and hence these oxides provide a good barrier for masking diffusions in integrated circuit fabrication.

High-pressure steam oxidations provide a means for growing relatively thick oxides in reasonable times at low temperatures to avoid dopant diffusion. Conversely, low-pressure oxidations show promise for forming controlled ultra thin gate growth for ULSI technologies.

Chlorine added to gate oxides [Sze, 1988] has been shown to reduce mobile ions, reduce oxide defects, increase breakdown voltage, reduce fixed oxide charge and interface traps, reduce oxygen-induced stacking faults, and increase substrate minority carrier lifetime. Chlorine is introduced into dry oxidations in less than 5% concentrations as anhydrous HCl gas or by trichloroethylene (TCE) or trichloroethane (TCA).

Dopant Segregation and Redistribution

Since silicon is consumed during the oxidation process, the dopant in the substrate will redistribute due to segregation [Wolf and Tauber, 1986]. The boundary condition across the Si/SiO₂ interface is that the chemical potential of the dopant is the same on both sides. This results in the definition of a segregation coefficient, m , as the ratio of the equilibrium concentration of dopant in Si to the equilibrium concentration of dopant in SiO₂. Depending on the value of m (i.e., less than or greater than 1) and the diffusion properties of the dopant in SiO₂, various redistributions are possible. For example, $m \approx 0.3$ for boron and it is a slow diffuser in SiO₂, so it tends to deplete from the Si surface and accumulate in the oxide at the Si/SiO₂ interface. Phosphorus, on the other hand, has $m \approx 10$, is also a slow diffuser in SiO₂, and tends to pile up in the Si at the Si/SiO₂ interface. Antimony and arsenic behave similarly to phosphorus.